# Study on the chromium (VI) formation in leather after ageing

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**Abstract:** Customer of tanneries and in particular footwear manufacturers currently ask even more often their leather supplier (tanners) for the evaluation of chromium VI presence after ageing of the leather (80°C, 24 h, R.H. 0-20%).

This request originated also from a recent draft test method prepared by the Technical Committee CEN/TC 309 "Footwear" concerning the assessment of the propensity of chromium VI formation in footwear and footwear components (leather, coated leather, leather fibre board).

Therefore, the aim of our research is to verify the possibility of chromium (VI) formation of semi-finished (wet-blue and crust) and finished leather by the use of two types of artificial ageing: "dry ageing" conduced in oven at different temperature conditions, 40°C, 60°C and 80°C and "wet ageing" in a climatic room with temperature control (40°C, 60°C, 80°C) and a given relative humidity (20%).

The presence of chromium (VI) after artificial ageing has been also evaluated in leather samples stored for a definite time (72 h, 120 h, 288 h) at room temperature (16-20°C) and around 60-70% relative humidity.

The analytical results allow to state following considerations:

- in crust and finished leather the chromium (VI) formation rises in accordance to the temperature increase
- instead, in the investigated wet-blue, chromium (VI) is nor present at the temperature of 80°C
- in general the "dry ageing" lead to a higher quantity of chromium (VI) formation in comparison to the "wet ageing" test method

  the leather samples artificially "aged" after conditioning at room temperature, show a reduction of the chromium (VI) content as regards the samples directly submitted to the ageing test

**Key words**: chromium (VI), ageing, chemical analysis, physical test, storage

## Introduction

The formation of hexavalent chromium from trivalent chromium can be due to three main reasons: oxidation in air presence, at high pH values;

1. ageing: oxidation in air presence when the leather is subject to the exposure of the solar light;
2. thermal ageing: oxidation in air presence when the leather is subject to the action of the heat.

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3. Probably based on such reasons, CEN/TC 309 “Footwears” has recently developed a test method to assess the propensity to chromium (VI) formation in footwear materials (leather, covered leather, etc) after ageing.

The ageing conditions of the method regard the temperature (80°C), the relative humidity, comprised between 0 and 20%, and the duration (24 hours).

It seems obvious that this artificial ageing is an attempt to accelerate the conversion of trivalent chromium to hexavalent, as it’s note that the rate of a chemical reaction increases with temperature, according to Arrhenius law. In short, by measuring hexavalent chromium before and after the artificial ageing, it’s possible to estimate if the treatments carried out for the leather production have an effect in oxidation of trivalent chromium.

In this work, the method proposed by CEN/TC 309 has been applied on wet blue, crust and finished leathers; at the same time using the same procedure of method CEN/TC 309, two temperature have been tested (40°C and 60°C). Further tests have been carried out in oven (“ageing in dry conditions”) setting temperature conditions at 40°C, 60°C and 80°C.

The formation of Chromium VI has been also estimated at different ageing times and in particular after 2 hours and 24 hours.

At last the evaluation of Chromium VI has been made also after conditioning of the leather samples deriving from ageing.

**Experimental**

For the ageing tests, wet-blue, crust and finished sheepskins and bovine leather have been used. The wet blue and crust leathers have been supplied by various tanneries of Solofra tanning district, while the finished leathers have been selected from the market.

The wet ageing tests have been carried out by a climatic chamber, NUVE ID 300, able to control temperature in a range from – 40 °C to 150 °C and relative humidity in a range from 15% to 98% for temperature limits from 10 °C to 90 °C.

The conditions set for the ageing tests have been the following:

T=40°C, 60°C, 80°C

R.H. = 20%

Time = 24 h

The dry ageing tests have been carried out by a ventilated oven, HERAEUS- VITTADINI. The test conditions have been the following:

T =40°C, 60°C, 80°C

Time = 24 h

The ageing tests according to the time have been carried out in wet conditions by the use of climatic room

with the following conditions:

T =80°C

R.H. = 20%

Time = 2 h and 24 h

The determination of Chromium VI has been carried out according to ISO 17075:2007 method; after ageing in climatic room the treated samples have been stored in laboratory with temperature and relative humidity conditions varying in the range 16-20 °C and 60-70% Hr respectively.

**Results**

In table 1 the analytical results for the wet blue skins are reported; as it is possible to notice, in no test, both on tal qualis and aged samples, Chromium VI presence has been found, probably as wet blue skins have generally low grease content and low pH values (inferior to 4).

**Table 1 Chromium VI in the skins wet blue**

| Sample | Tal qualis ppm | After Ageing | |
|---|---|---|---|
| | | Climatic chamber (80°C, 20% RH, 24h) | Oven 80°C, 24h |
| | | Ppm | ppm |
| Wet blue To | < 3 | < 3 | < 3 |
| Wet blue B | < 3 | < 3 | < 3 |
| Wet blue C | < 3 | < 3 | < 3 |
| Wet blue D | < 3 | < 3 | < 3 |

The results of the test on the crust leathers are shown in table 2;

**Table 2 Evaluation of Chromium VI on crust leather: tal qualis, after ageing in the climatic room and in oven**

| Sample | Tal qualis | Climatic chamber 20% RH - 24h | | | Oven 24h | | |
|---|---|---|---|---|---|---|---|
| | | 40°C | 60°C | 80°C | 40°C | 60°C | 80°C |
| | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Crust sheepskin | <3,0 | <3,0 | 4,0 | 5,6 | <3,0 | <3,0 | 15,0 |
| Chrome tanned with hair (with flesh-side embossed) | 3,1 | 5,1 | 6,6 | 11,7 | 4,8 | 7,0 | 13,3 |
| Finished bovine leather, chrome tanned | 18,5 | 18,5 | 18,5 | 23,5 | 18,5 | 18,5 | 25,7 |
| Laminated sheepskin | 8,5 | 10,8 | 12,2 | 16,0 | 8,5 | 8,5 | 24,6 |
| Embossed sheepskin | 4,4 | 6,9 | 10,7 | 18,4 | 6,7 | 8,6 | 19,8 |

The results can be summarized as follows:

- the Chromium VI formation is related to the temperature;
- more elevate values are obtained at 80°C, both in wet and in dry ageing;
- at ageing temperature of 40°C, instead, there is no significant raising of the values of Chromium VI;
- at ageing temperature of 80°C, the Chromium VI values, after dry ageing; are, generally, higher regarding those obtained in case of ageing in climatic room.

In Table 3, the results of evaluation of Chromium VI on samples treated for different times at the ageing conditions of the CEN/TC 309 method are reported:

**Table 3 Evaluation of Chromium VI according to the ageing time**

| Sample | Tal qualis | Climatic room R.H. 20% T =80°C t = 2h | Climatic room R.H. 20% T =80°C t = 24h |
|---|---|---|---|
| | ppm | ppm | ppm |
| Crust Sheepskin | <3,0 | <3,0 | 5,6 |
| Chrome tanned with hair (with flesh-side embossed) | 3,1 | 5,2 | 11,7 |
| Finished bovine leather, chrome tanned | 18,5 | 23,5 | 23,5 |
| Laminated sheepskin | 8,5 | 10,0 | 16,0 |
| Embossed sheepskin | 4,4 | 5,7 | 18,4 |

As it is possible to notice, the increase of Chromium VI concentration begins already after 2h, but the effect of ageing increases largely after 24 h of treatment, except for the bovine leather. It's interesting to underline that when the sample, before ageing, has Chromium VI concentration below the detection limit, the ageing time is a main variable for the conformity to the CEN/TC 309 method.

In order to estimate the influence of free Chromium on the formation of Chromium VI, the amount of extractable Chromium by water, acid perspiration (at pH = 5,5) and phosphate buffer has been correlated with the Chromium VI formation after ageing.

The data, reported in table 4, shows that the value of total extractable Chromium increases according to the pH; the extract by phosphate buffer at pH 8, carried out according to ISO 17075, presents the highest value of total extractable chromium. That, in various cases, exceeds 200 ppm. The values of extractable chromium by phosphate represent in most of cases approximately 1-2% of total chromium present in the chrome tanned leathers.

**Table 4 Comparison between the content of total extractable Chromium and the Chromium VI**

| Sample | Chromic Oxide % | Extractable Chromium by water (mg/kg) | Total extractable Chromium by acid perspiration (mg/kg) | Total extractable Chromium by phosphate buffer (mg/kg) | Chomium VI | |
|---|---|---|---|---|---|---|
| | | | | | t.q. ppm | 80°C ppm |
| Crust Sheepskin | 2,8 | 26,5 (pH=3,9) | 28,2 | 171,3 | <3,0 | 5,6 |
| Chrome tanned with hair (with flesh-side embossed) | 1,9 | 62,0 (pH=4,7) | 93,1 | 252,7 | 3,1 | 11,7 |
| Finished bovine leather, chrome tanned | 5,7 | 10,9 (pH=5,6) | 40,7 | 86,2 | 18,5 | 23,5 |
| Laminated sheepskin | 4,0 | 87,4 (pH=4,8) | 99,1 | 239,8 | 8,5 | 16,0 |
| Embossed sheepskin | 2,1 | 34,3 (pH=4,5) | 47,5 | 267,4 | 4,4 | 18,4 |

From the data reported in table 4, it is also possible to notice that a small percentage of extractable Chromium (approximately 1-3%) is already present as Chromium VI in the not-treated samples.

Analyzing the trend of pH of the water extract of the leathers versus the presence of the Chromium VI, we can notice that at higher pH values correspond higher Chromium VI concentrations, both in tal qualis and in aged samples; at the same time the entity of the generation of Chromium VI after ageing, respect to initial values of tal qualis leathers, seems to have an inverse correlation with the pH of leathers. In fact the bovine leather, that is less acid than others (pH=5,6), show the highest values of Chromium VI (18,5 ppm on tal qualis and 23,5 ppm after ageing), but the generation is limited (+27%) respect to the other leathers, in which the Chromium VI concentration at least duplicate after ageing.

The analytical results of the tests, carried out conditioning at 18°C and 65% R.H. the samples deriving from the ageing treatment for different periods (48 h, 72 h, 96 h, 120 h, 168 h and 288 h) and then determining the Chromium VI concentration according to ISO 17075, are reported in tables 5, 6 and 7.

**Table 5 Evaluation of Chromium VI after ageing in climatic room and conditioning**

| Sample | Tal qualis | Climatic room R.H.20%, 24h,60°C | After conditioning | Conditioning Time | Climatic room R.H.20%, 24h,80°C | After conditioning | Conditioning Time |
|---|---|---|---|---|---|---|---|
| | ppm | ppm | ppm | h | ppm | ppm | h |
| Crust Sheepskin | <3,0 | 4,0 | 3,5 | 48 | 5,6 | 5,1 | 72 |
| Chrome tanned with hair (with flesh-side embossed) | 3,1 | 6,6 | 6,0 | 96 | 11,7 | 8,7 | 120 |
| Finished bovine leather, chrome tanned | 18,5 | 18,5 | 19,8 | 96 | 23,5 | 23,3 | 120 |
| Laminated sheepskin | 8,5 | 12,2 | 10,3 | 96 | 16,0 | 15,6 | 96 |
| Embossed sheepskin | 4,4 | 10,7 | 6,5 | 96 | 18,4 | 12,0 | 96 |

**Table 6 Evaluation of Chromium VI after ageing in oven and conditioning**

| Sample | Tal qualis | Oven 24h,60°C | After conditioning | Conditioning Time | Oven 24h,80°C | After conditioning | Conditioning Time |
|---|---|---|---|---|---|---|---|
| | ppm | ppm | ppm | h | ppm | ppm | h |
| Crust Sheepskin | <3,0 | / | / | / | 15,0 | 11,1 | 96 |
| Chrome tanned with hair (with flesh-side embossed) | 3,1 | 7,0 | 6,9 | 48 | 13,3 | 9,9 | 120 |
| Finished bovine leather, chrome tanned | 18,5 | 18,5 | 16,9 | 48 | 25,7 | 20 | 120 |
| Laminated sheepskin | 8,5 | 8,5 | 6,9 | 48 | 24,6 | 16,4 | 72 |
| Embossed sheepskin | 4,4 | 8,6 | 8,8 | 48 | 19,8 | 15,7 | 72 |

**Table 7 Evaluation of Chromium VI after ageing in oven and longer conditioning**

| Sample | Tal qualis | Oven 24h, 80°C | Conditioning 288h | Chromium VI Variation |
|---|---|---|---|---|
| | ppm | ppm | ppm | % |
| Crust Sheepskin | <3,0 | 15,0 | 7,9 | -47,3 |
| Laminated sheepskin | 8,5 | 24,6 | 12,6 | -48,8 |
| Embossed sheepskin | 4,4 | 19,8 | 9,1 | -54,0 |

The data generally evidences the decreasing of the Chromium VI after conditioning, but in no case the content returns to the value before ageing. As expected, the lessening of Chromium VI content is more notable after high period of conditioning, near 50% after 288 h.

**Conclusions**

Chromium is one of more interesting metals under the alimentary, environmental and toxicological point of view, and the chrome tannage is surely the most important for the production of leathers for footwear, furniture and apparel.

The possible formation of Chromium VI in the leather could have a great influence on the production of the European and also world-wide tanneries.

During last years, many alternative procedures have been searched and proposed, but they are not able to guarantee the effective substitution of the chrome tannage.

Currently, customers, and in particular footwear industry, requires more and more to the tanneries the evaluation of the presence of Chromium VI after ageing of the leather at 80°C and R.H. 0-20% for 24h. These conditions derive from a recent draft standard method developed by CEN/TC 309 “Footwears” to assess the propensity to chromium (VI) formation in footwear materials (leather, covered leather, etc) after ageing.

Therefore, this work wants to verify the possibility of Chromium VI formation in the semifinished (wet blue and crust) and finished leathers as a result of the artificial ageing.

The obtained results evidenced that:

- The ageing method proposed by CEN/TC 309 “Footwears” is not realistic as:
    - ageing conditions (T = 80°C, t = 24h) are too much drastic,
    - they don’t simulate the conditions of use of leather,
    - they don’t simulate the conditions of footwears production;
- The wet-blue leathers don’t show propensity of Chromium VI formation;
- The majority of finished leathers have propensity at Chromium VI formation after ageing;

- The trivalent chromium of the retannage process, more weakly linked to the collagen than chromium III fixed in tanning, could have an active role in the Chromium VI generation;
- If the artificial ageing is followed by a conditioning period, the Chromium VI content in the leather samples decreases according to the time.

**References**

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